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Reaction of Curium(III) Ions with Oxo-species in Alkali Chloride Melts

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Electronic absorption spectra of curium(III) chloro-species were measured in 3LiCl-2KCl (at 450 °C) and NaCl-2CsCl (at 550, 650 and 750 °C) eutectic melts and the molar absorption coefficients determined. The effect of oxide species addition to the melt on the absorption spectra of curium was studied. A new species, evident from the absorption bands around 360 nm, is formed when barium oxide is dissolved in the melt or O_2-Cl_2 or Ar-HCl-H_2O gas mixtures bubbled through. This species is ascribed to soluble curium oxychloride. It does not react with chlorine bubbled through the melt unless there is carbon present.

Introduction

Pyrochemical reprocessing of spent nuclear fuels employing alkali metal chloride based melts is considered as a possible alternative to the existing extraction technology. Curium is one of the minor actinides present in the spent fuel and understanding its behavior in molten salts is important for designing a feasible process. The stable oxidation state of curium in chloride melts is +3. The electrochemical studies in NaCl-2CsCl melt showed that $CmCl_6^{3-}$ species undergo a one-step three-electron reduction to Cm(0) (1). No evidence of higher oxidation states of curium in this melt was obtained.

Similar to lanthanides, trivalent curium forms a stable oxychloride CmOCl, *e.g.*, by reacting $CmCl_3$ (or Cm_2O_3) at 500–600 °C with vapor in equilibrium with a 10 M solution of HCl (2). The crystal structure of CmOCl has also been characterized (2). Formation of curium oxychloride is possible in molten salts. The interaction of Cm(III) chloride with oxygen species in fused alkali chlorides was recently studied electrochemically (3). Depending on the concentration of oxide ions, melt composition and temperature curium oxychloride or oxide may be formed:

$$Cm^{3+} + O^{2-} + Cl^- \rightarrow CmOCl \quad [1]$$
$$2\ Cm^{3+} + 3\ O^{2-} \rightarrow Cm_2O_3 \quad [2]$$

Electronic absorption spectroscopy can be applied for studying behavior of Cm(III) ions having $5f^7$ electronic configuration. Electronic absorption spectra (EAS) of Cm(III) and (IV) species have mostly been studied in solutions and in the solid state (4-8). A recent EXAFS spectroscopy study showed that in dilute aqueous chloride solutions (0.25 M HCl) Cm^{3+} ions are surrounded by H_2O molecules with the hydration number just over ten (9). In concentrated (10.5 and 12.3 M) solutions of LiCl the hydration number decreases to 6.6-6.1 and Cl^- enters the inner coordination sphere with the coordination

number 2.1-2.4. A very limited body of work exists on the spectra of curium in melts. EAS of molten $Cs_2NaCmCl_6$ were recorded at 830 ^oC as well as the spectra of solutions of curium(III) chloride in (Li-Na-K)F and (Li-Na-K)(Cl-F) mixtures at 650 ^oC (10,11). In all molten salt systems studied the spectra were interpreted as arising from six-coordinated octahedral Cm(III) species. In the present work the electronic absorption spectroscopy was employed to study the reactions of Cm(III) containing chloride melts with oxygen species.

Experimental

The experiments were conducted in two eutectic melts, NaCl-2CsCl at 550-750 ^oC and 3LiCl-2KCl at 450 ^oC. Curium-244 isotope was used throughout the study. The starting curium(III) chloride containing melts were prepared by chlorinating curium dioxide (purified from plutonium and americium using standard techniques) in a chosen solvent melt. Owing to relatively low molar absorption coefficients of Cm(III) in fused chlorides the concentration of curium in the melts used here for the spectroscopy measurements varied from 0.1 to 0.3 mol/l and the total amount of curium used in a single experiment ranged from 0.10 to 0.37 g. The melts were held in silica cells with 1 cm path length optical parts attached to the bottom. The cells accommodated gas bubbling tubes and other required accessories. All manipulations with the experimental cells were conducted in a negative pressure glove box with an optical furnace attached to the bottom. The EAS were measured using a double channel fiber optic spectrometer AvaSpec-2048-2 (Avantes).

Oxide species were introduced into the melt by adding barium oxide or bubbling gaseous mixtures (Cl_2-O_2 or HCl-H_2O-Ar) with various partial pressures of the components according to the following equilibria:

$$\tfrac{1}{2}\, O_{2\,(g)} + 2\, Cl^- \leftrightarrow O^{2-} + Cl_{2\,(g)} \quad [3]$$

$$2\, H_2O_{\,(g)} + 4\, Cl^- \leftrightarrow O^{2-} + 4\, HCl_{\,(g)} \quad [4]$$

Results and discussion

Absorption spectra of Cm(III) ions in fused chlorides

The EAS of curium(III) chloride solutions in NaCl-2CsCl and 3LiCl-2KCl eutectic melts are shown in Figure 1. Profile of the spectral curves and the absorption bands present correspond to those reported for six-coordinated $CmCl_6^{3-}$ species (11). Primary maxima in the spectra are situated at *ca.* 435-445, 405 and 380-390 nm. The EAS recorded in NaCl-2CsCl melt at 550-750 ^oC and in 3LiCl-2KCl melt at 450 ^oC are similar, with the molar absorption coefficient somewhat increasing from NaCl-2CsCl to 3LiCl-2KCl. Weak absorption peaks around 500 nm resulted from a minor americium(III) impurity present. The concentration of americium can be estimated from the known molar absorption coefficients of Am(III) ions in alkali chloride melts (12). In the present study the Am : Cm molar ratio in the melts did not exceed 0.004.

The absorption spectra of $CmCl_6^{3-}$ complex ions were resolved into individual bands and an example is given in Figure 2 with the electronic transitions corresponding to the individual bands marked. The transitions observed arise from the ground $^8S_{7/2}$ state.

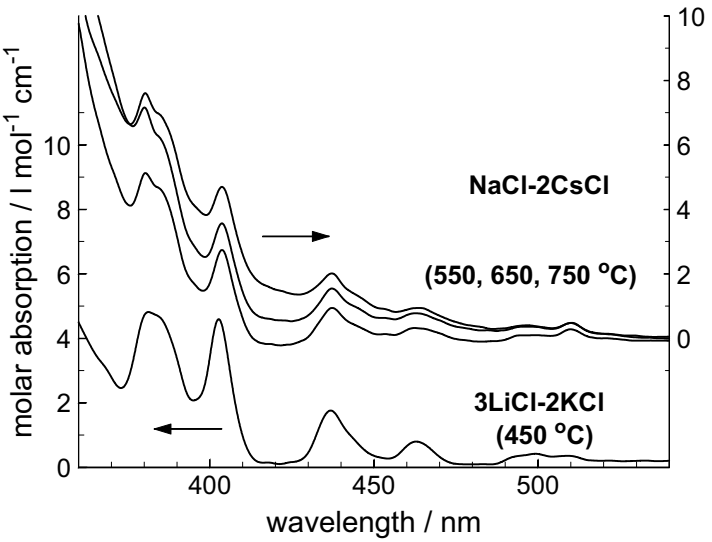

Figure 1. EAS of Cm(III) chloro-species in NaCl-2CsCl and 3LiCl-2KCl eutectic melts. Temperature (top to bottom): 550, 650, 750, and 450 °C.

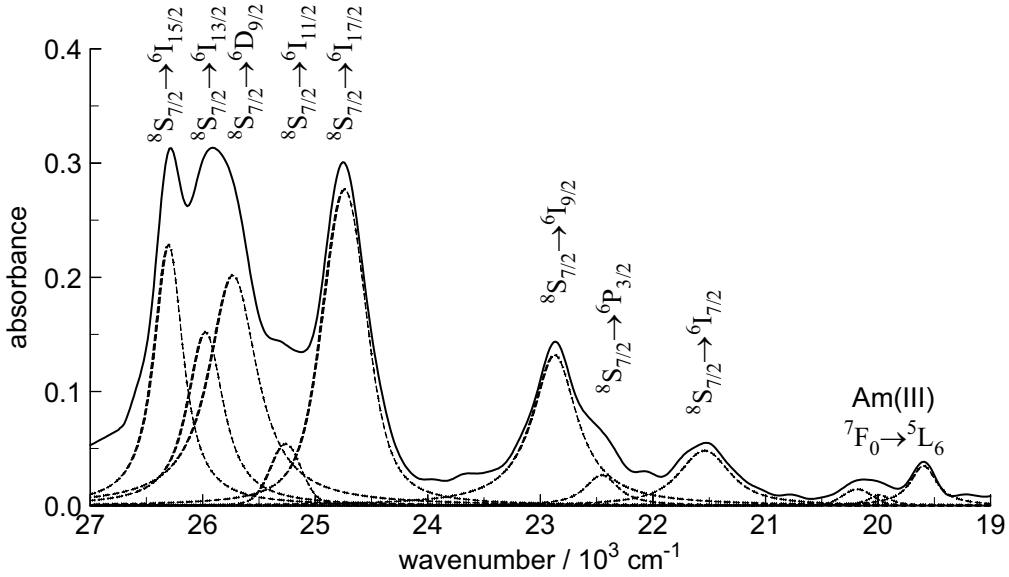

Figure 2. Electronic absorption spectrum of $CmCl_6^{3-}$ in NaCl-2CsCl eutectic melt at 550 °C resolved into individual bands (background subtracted) with the corresponding electronic transitions marked. $[Cm^{3+}] = 0.115$ mol/l. Peaks around 19500-20500 cm^{-1} arise due to some Am impurity present in starting curium oxide.

The Cm–Cl distance (R_{Cm-Cl}) in $CmCl_6^{3-}$ was estimated employing a procedure described by Barbanel (11). In 3LiCl-2KCl melt at 450 °C R_{Cm-Cl} equaled to *ca.* 0.275 nm. In NaCl-2CsCl melt R_{Cm-Cl} was around 0.270 nm and varying the temperature (from 550 to 750 °C) did not have any noticeable effect on the value of R_{Cm-Cl}. The values of Cm–Cl distance obtained here agree well with the results reported for molten $Cs_2NaCmCl_6$ at 830 °C, 0.272 nm and for the solutions of $CmCl_3$ in 8.7-12.3 M LiCl at room temperature, 0.275-0.276 nm (9,11). For comparison, in solid $Cs_2NaCmCl_6$ at 680 °C $R_{Cm-Cl} = 0.268$ nm (11).

Reaction of Cm(III) species with oxide ions

To study the effect of oxygen on speciation of curium(III) in fused alkali chlorides, a melt containing 0.045 mol/l of $CmCl_6^{3-}$ in NaCl-2CsCl at 550 °C was sparged with chlorine-oxygen mixtures. The partial pressure of O_2 was gradually (in ten successive steps) increased from 0.0250 to 0.9937 atm, and the bubbling tube was made of silica. Unfortunately chlorine dissolved in the melt prevented measuring reasonable quality spectra below 480 nm due to high absorbance, even when the partial pressure of Cl_2 was as low as 0.0063 atm. After the melt was sparged with argon (to remove dissolved chlorine) a spectrum could be recorded and that contained a peak at around 360 nm not previously present, Figure 3.

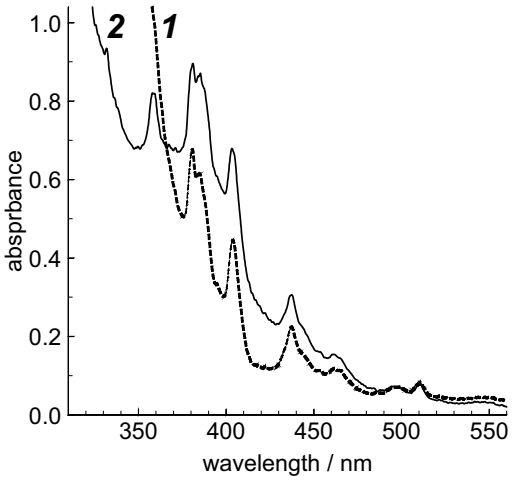

Figure 3. EAS of Cm(III) in NaCl-2CsCl eutectic melt at 550 °C before (line 1) and after (line 2) sparging the melt with Cl_2-O_2 gas mixtures.

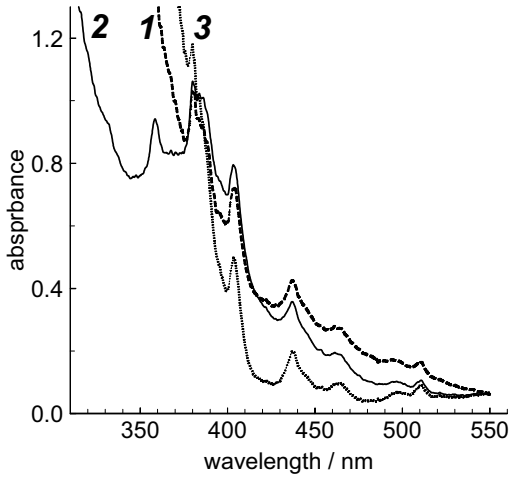

Figure 4. Effect of adding barium oxide on EAS of Cm(III) in NaCl-2CsCl eutectic melt at 550 °C: starting melt (line 1); after adding BaO and bubbling Cl_2 followed by Ar through a silica tube (line 2); and after bubbling Cl_2 followed by Ar through a graphite tube (line 3).

Another method of introducing oxygen species into the melt was addition of barium oxide. After adding 0.010 g of BaO to a NaCl-2CsCl melt containing 0.156 g of $CmCl_3$ the resulted mixture was held for 30 min and then the turbid melt was sparged with Cl_2 for 15 min followed by argon for another 15 min. Chlorine and argon were bubbled through a silica capillary tube dipped into the melt. After such manipulation the spectrum of the starting melt (line 1 in Figure 4) changed and a well defined peak around 360 nm appeared (line 2 in Figure 4). Resulting melt was further sparged with Cl_2 for 15 min but this time the gas supplying tube was made of graphite. After removing excess dissolved chlorine by bubbling argon for 15 min through the melt the spectrum recorded (line 3 in Figure 4) closely resembled that of the starting $CmCl_6^{3-}$ containing melt and the peak at 360 nm was no longer present.

Thus the new peak around 360 nm in the EAS of curium containing melts appears after O^{2-} ions are introduced into the system. This peak remains unchanged after the melt is sparged with gaseous chlorine supplied through a silica tube but disappears if Cl_2 is

bubbled through a graphite tube. This peak cannot be ascribed to the transitions in $CmCl_6^{3-}$ ion. The absorption spectrum of Cm^{3+} aqueous acidic solutions contains a band at 352 nm originating from $^8S_{7/2} \rightarrow {}^6D_{7/2}$ transition but the intensity of this band is very low (the oscillator strength is *ca.* 50 times below that of the band at 395 nm) (8). The peak appearing in the spectra of chloride melts at 360 nm is currently ascribed to the soluble curium(III) oxychloride formed by the reaction [1], and the following reactions describe its behavior in the presence of chlorine:

$$CmO^+ + Cl_2 \rightarrow \text{no reaction} \quad [5]$$

$$2\ CmO^+ + 2\ Cl_2 + C \rightarrow 2\ Cm^{3+} + CO_2 + 4\ Cl^- \quad [6]$$

The EAS of the melts containing Cm(III) chloro-species and the proposed CmO^+ ions (with background and the charge transfer band subtracted) are compared in Figure 5.

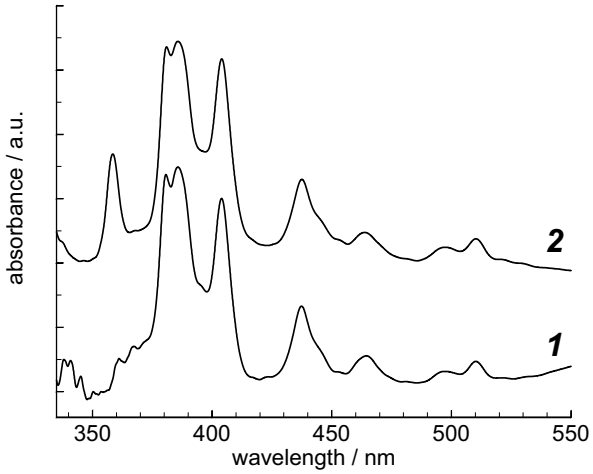

Figure 5. Electronic absorption spectra of NaCl-2CsCl melt containing Cm(III) species before (line 1) and after (line 2) introducing oxide ions, 550 °C.

For a more detailed study of the behavior of curium(III) species in chloride melts in the presence of O^{2-} ions the concentration of the oxide ions in the melt was varied by bubbling through the melt Ar-HCl-H_2O gas mixtures with different partial pressures of the components. The equilibrium of the reaction [4] depends on the ratio of partial pressures of HCl and H_2O. In the present work the value of $\log\left(p_{HCl}^2 / p_{H_2O}\right)$ in the gas mixtures was varied between 0.5 and -10.6.

Bubbling Ar-HCl-H_2O gas mixtures through the 3LiCl-2KCl eutectic containing $CmCl_3$ at 450 °C resulted in gradual changes in the EAS as the partial pressure of water increased, Figure 6. The absorbance below 400 nm decreased and a peak around 360 nm appeared. From the known value of the equilibrium constant for the reaction [4]:

$$K = \frac{p_{HCl}^2 \cdot [O^{2-}]}{p_{H_2O} \cdot [Cl^-]^2} \quad [7]$$

the concentration of the oxide ions in the melt can be estimated. For 3LiCl-2KCl melt at 450 °C K equals to *ca.* 10.29-10.33 (13-15).

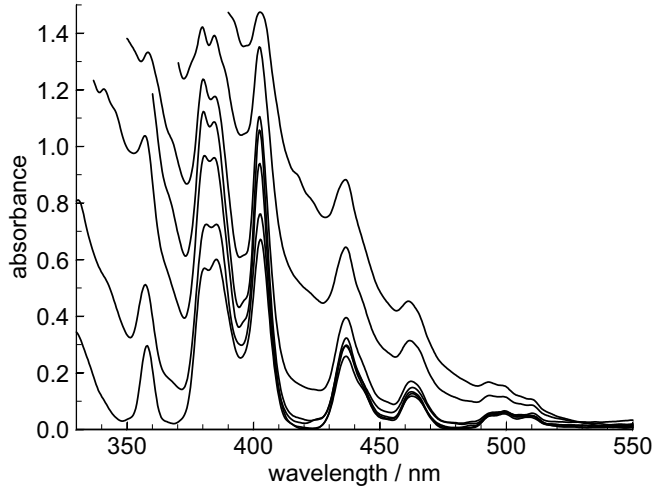

Figure 6. Changes in the EAS of 3LiCl-2KCl melt containing Cm(III) species after bubbling Ar-HCl-H_2O gas mixtures at 450 °C. Values of $\log\left(p_{HCl}^2 / p_{H_2O}\right)$ in the gas phase (top to bottom): 0.49, -1.31, -2.31, -3.31, -4.47, -5.38 and -6.39. Starting Cm(III) concentration 0.158 mol/l.

After the value of $\log\left(p_{HCl}^2 / p_{H_2O}\right)$ dropped below -5.4 (corresponding to p[O^{2-}] value below 5) some solid phase started to form in the melt. This was detected from the growing background in the spectra in the entire wavelength region. This solid is currently attributed to curium oxide (reaction [2]) although it cannot be excluded that the solubility of CmOCl was exceeded and the excess of oxychloride precipitated. When the final melt with p[O^{2-}] around unity was sparged with chlorine using a graphite tube all the solids were dissolved, the peak at *ca*. 360 nm disappeared and the EAS returned to the initial state (upper line in Figure 6). The relative amounts of different curium species were estimated from the results of the spectroscopy measurements and the results are presented in Figure 7.

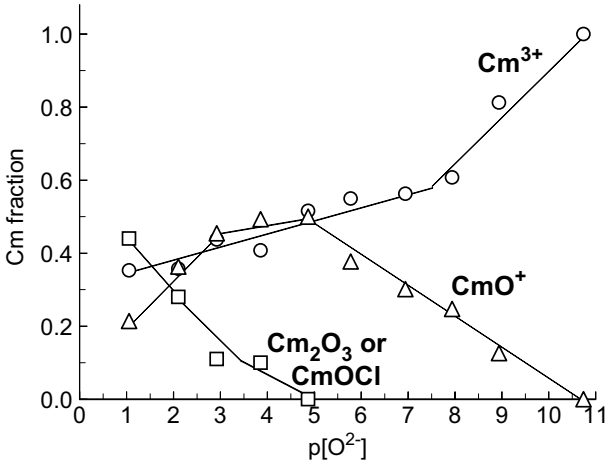

Figure 7. Distribution of curium between various species in 3LiCl-2KCl melt at 450 °C estimated from the results of EAS measurements at various compositions of the gaseous mixture (Ar-HCl-H_2O) bubbled through the melt. Total molar fraction of Cm in the melt is 0.0059.

Changes in the EAS of curium containing NaCl-2CsCl melts during bubbling Ar-HCl-H_2O mixtures at 550, 650 and 750 ^oC were similar to those observed in 3LiCl-2KCl eutectic. An example of the spectra recorded at 550 ^oC is given in Figure 8. At all the temperatures studied a peak around 360 nm appeared as the partial pressure of H_2O in the gas mixture increased and that peak disappeared after chlorine was bubbled through the melt using a graphite tube or a silica tube with a graphite thread suspended inside.

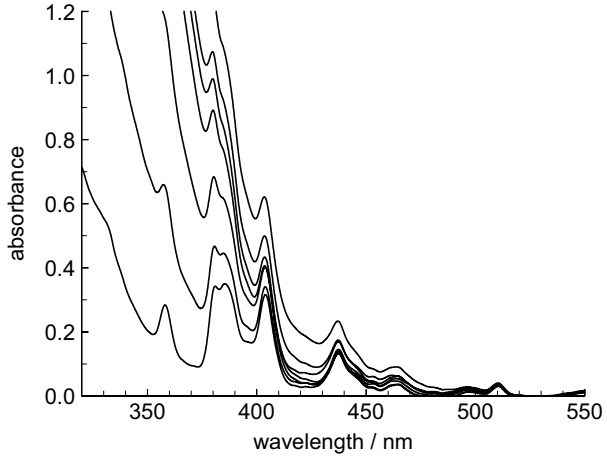

Figure 8. Changes in the EAS of NaCl-2CsCl melt containing Cm(III) species after bubbling Ar-HCl-H_2O gas mixtures at 550 ^oC. Values of $\log\left(p_{HCl}^2 / p_{H_2O}\right)$ in the gas phase (top to bottom): -1.4, -2.1, -2.9, -3.6, -4.3, -5.0 and -5.7. Starting Cm(III) concentration 0.115 mol/l.

There is no data on the equilibrium constant for the reaction [4] in NaCl-2CsCl melts to enable calculation of the oxide ions concentration in the melt. Analysis of intensities of the absorption peaks in the EAS shows that in NaCl-2CsCl melt the concentration of Cm^{3+} ions initially decreased, then leveled off. Concentration of CmO^+ mirrored that of Cm^+. No formation of a solid precipitate was noted. The preliminary results concerning distribution of curium species in NaCl-2CsCl melt at various ratios of HCl and H_2O in the gas phase are presented in Figure 9.

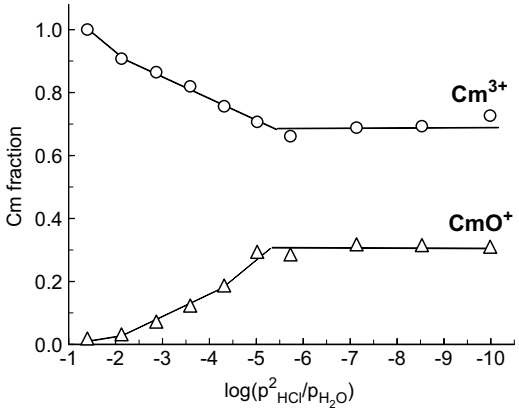

Figure 9. Distribution of curium between various species in NaCl-2CsCl melt at 550 ^oC obtained from the results of EAS measurements at various compositions of the gaseous mixture (Ar-HCl-H_2O) bubbled through the melt. Total molar fraction of Cm in the melt is 0.0058.

Conclusions

The electronic absorption spectra of curium(III) chloro-species, $CmCl_6^{3-}$, were recorded in chloride melts based on 3LiCl-2KCl and NaCl-2CsCl eutectics between 450 and 750 ^oC. The absorption bands in the spectra arise from the electronic transitions from the ground $^8S_{7/2}$ state. The Cm-Cl distance estimated from the results of spectroscopy measurements is 2.75 Å in 3LiCl-2KCl melt and 2.70 Å in NaCl-2CsCl melt. In the presence of oxide species (added to the melt by dissolving barium oxide or by bubbling Cl_2-O_2 or Ar-HCl-H_2O gas mixtures) the absorbance below 400 nm decreases and a new peak (tentatively attributed here to the soluble curium oxychloride) around 360 nm appears. This peak becomes more pronounced as the concentration of O^{2-} in the melt increases. Bubbling pure Cl_2 through the melt does not affect this peak but in the presence of carbon (*e.g.*, using a graphite tube for introducing Cl_2 into the melt) the absorption peak around 360 nm disappears. The results of the spectroscopy measurements were applied here to obtain some preliminary estimates of curium species distribution in alkali chloride melts depending on the concentration of oxide ions.

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